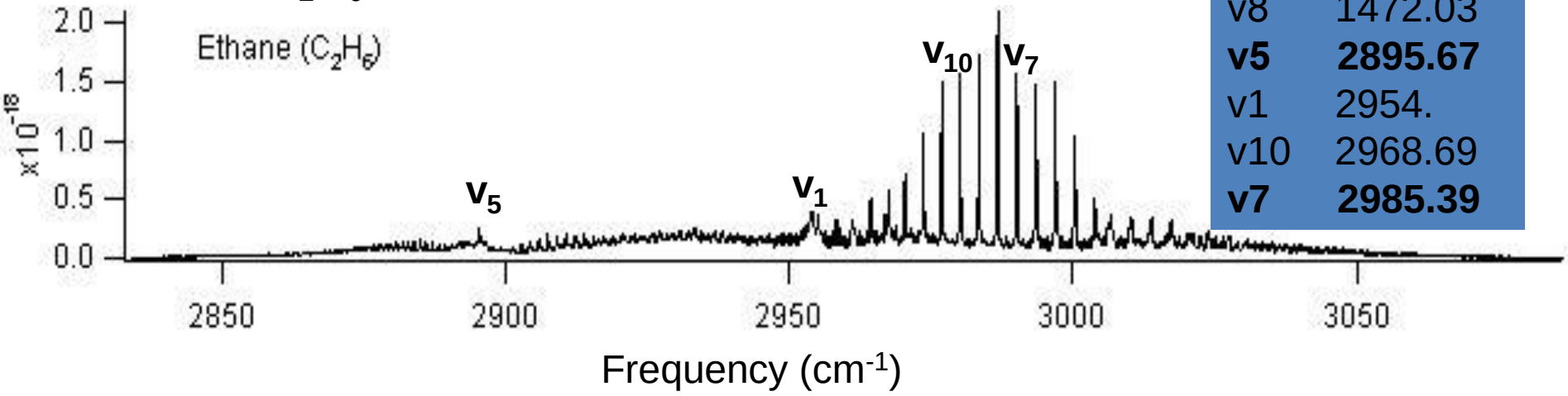
Ethane Spectroscopy 2850-3050 cm^{-1}

Ethane is a strong absorber in the troposphere. The 2950-3020 cm^{-1} region contains the strongest C_2H_6 absorptions in the infrared. Line depths can exceed 50% along limb paths in the tropical troposphere.

Ethane has a complicated spectrum (many interacting vibrational modes), which makes it difficult to accurately predict the spectrum. The 2900 cm^{-1} region is very messy with 4 interacting fundamentals, 2 IR-active and 2 inactive.

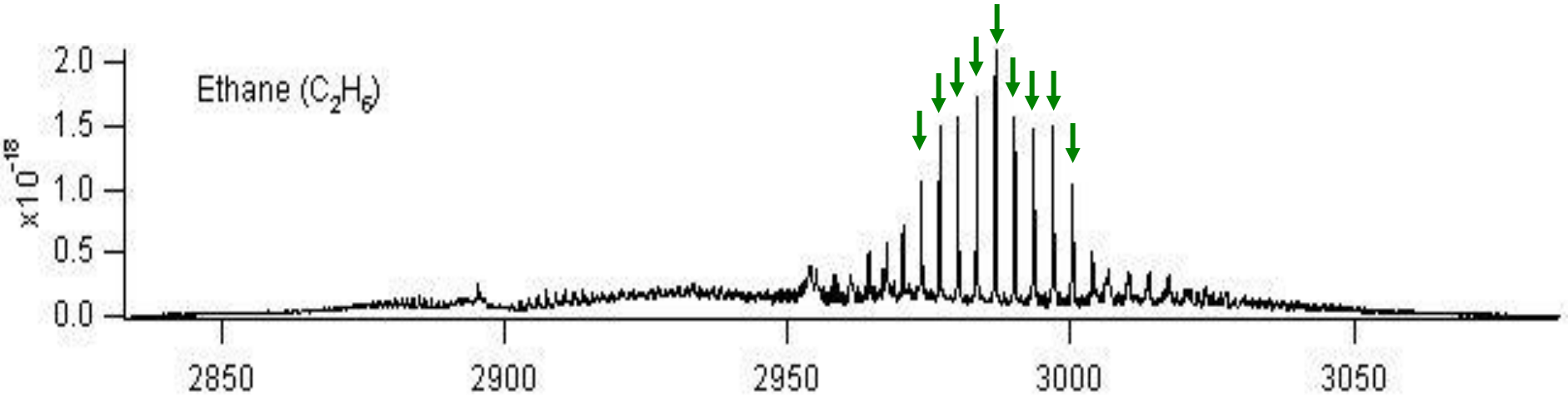
Mode	Freq
v4	289.32
v9	**822.72**
v3	995.11
v12	1195.3
v6	**1379.16**
v2	1397.
v11	1468.1
v8	1472.03
v5	**2895.67**
v1	2954.
v10	2968.69
v7	**2985.39**

A C_2H_6 laboratory spectrum (PNNL).



Spectroscopy History

- Pine & Lafferty (1982, 1984) assigned C_2H_6 transitions from spectra acquired at 156K, but didn't include PQ-branches
- In 1985, in support of ATMOS, Linda Brown developed an empirical linelist for the 9 strongest PQ-branches of C_2H_6 covering 2973-3001 cm^{-1} (↓).
- Pine and Rinsland [1999] developed a quantum-mechanically-based linelist for the PQ_3 branch at 2976 cm^{-1}. This was included in HITRAN_2004.
- PNNL measured C_2H_6 cross-sections from 700-6500 cm^{-1} at 0.1 cm^{-1} res.
- July 2007 HITRAN C_2H_6 update contains the Pine & Rinsland PQ_3 branch, together with Brown's empirical linelist for the other PQ-branches.
- In 2008/9 Harrison & Bernath measure C_2H_6 at many T/P at RAL



Overview

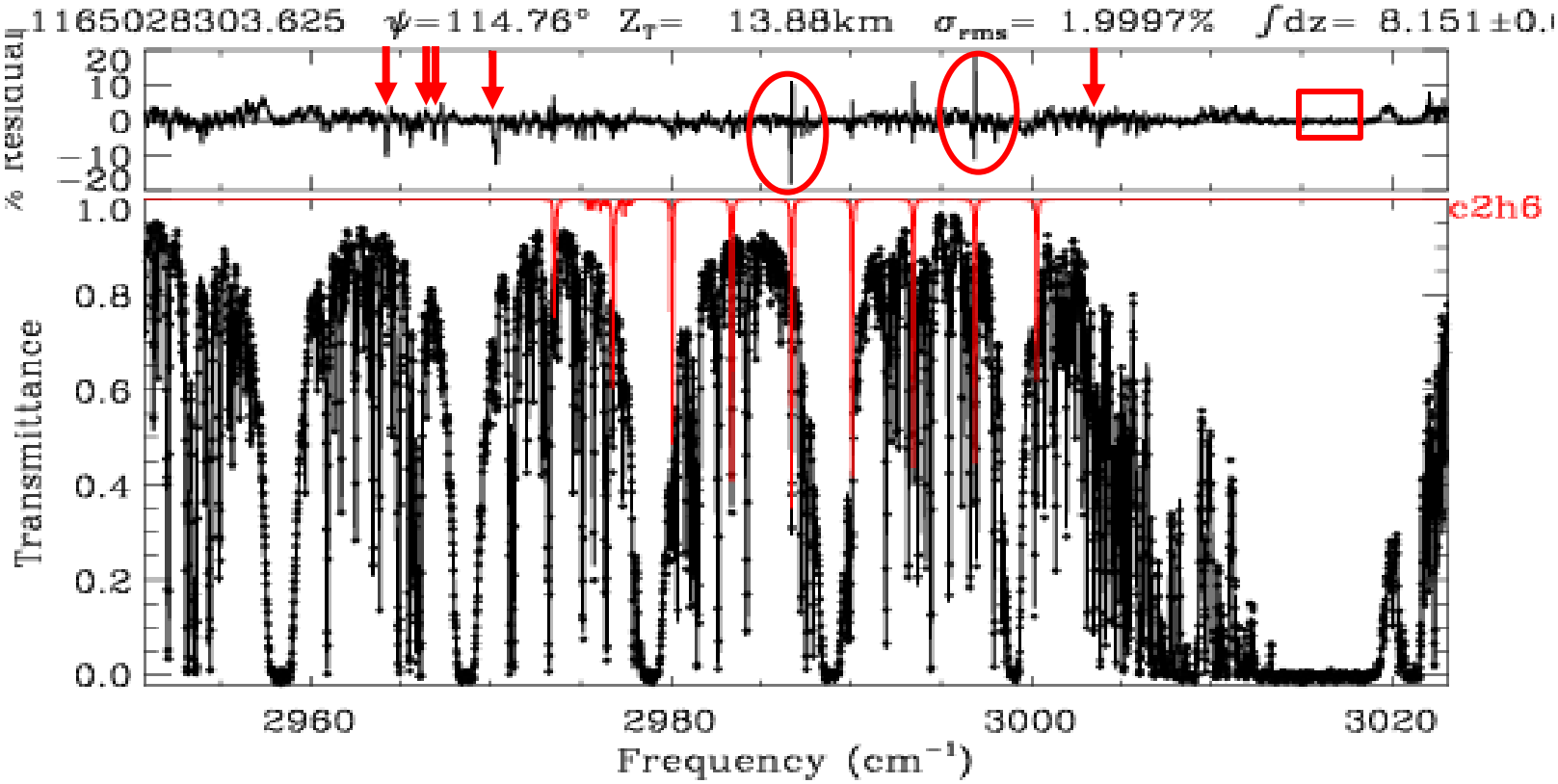
This presentation will examine the July 2007 HITRAN C_2H_6 update linelist, which is used in HITRAN 2008. Although it is much improved in the 820 cm^{-1} region, it is inadequate in the 2950-3020 cm^{-1} region where many gases of interest have absorption bands:

Specific problems include:
1) Omission of weaker PQ-branches (below 2973 cm^{-1}; above 3001 cm^{-1})
2) All P- and R-branch lines are missing

An empirical C_2H_6 Pseudo-Line List (PLL) was developed based on lab measurements made at RAL by Jeremy Harrison and Peter Bernath. The PLL is compared with HITRAN using laboratory and atmospheric spectra.

Fits to ACE Spectra – HITRAN 2008

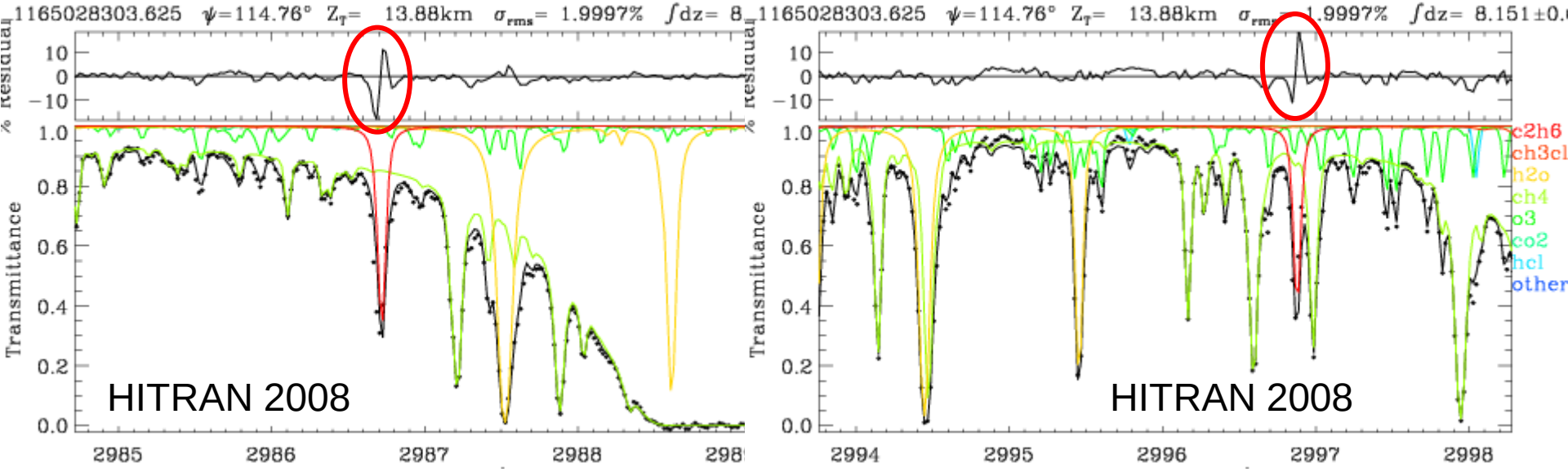
Fit to an ACE spectrum acquired at 13.88 km tangent altitude in the tropics.
Strongest absorptions due to CH_4, H_2O, O_3, and C_2H_6 (red).



Largest residuals due to the 2986 and 2997 cm^{-1} C_2H_6 PQ-branches (red circles)
Residuals also seen due to missing PQ-branches (Red arrows).
Noise level is about 0.3% (Red rectangle), so residuals are mainly systematic.

Investigate the two largest residuals

The plots below zoom in on the two largest residuals of the previous figure. The other absorbing gases are included by color.

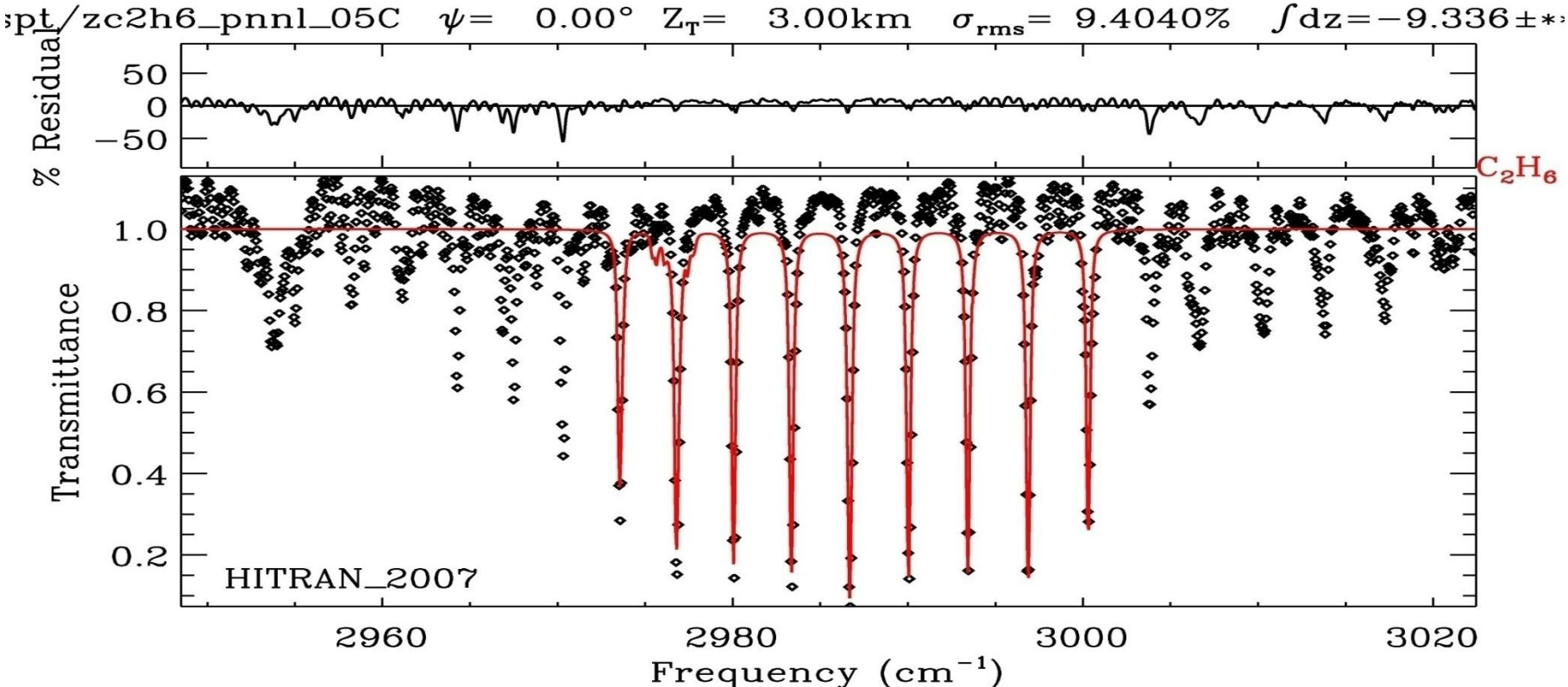


There seems to be shifts in the position of these two PQ-branches, and also width errors.

Spectral fits to PNNL Spectra

How do I know that the missing absorptions in the ACE occultation spectra are due to C_2H_6 and not some other gas?

I fitted 0.1 cm^{-1} resolution PNNL (Pacific NorthWest National Laboratory) spectra of pure C_2H_6 using the same linelists used to fit the ACE spectra.



An empirical C_2H_6 Pseudo-linelist covering 2720-3100 cm^{-1}

To better understand the C_2H_6 spectrum at 2720-3100 cm^{-1}, laboratory measurements we're made at RAL under a variety of conditions.

This work is published as:

Jeremy J. Harrison, Nicholas D. C. Allen, and Peter F. Bernath,
Infrared absorption cross-sections for ethane (C2H6) in the 3 um region,
JQSRT, 111, 357–363, 2010

Spectrum	v_start	v_end	Npts	T	tot_pres	p_pres	cell_length	OPD
"C2H6_PURE_295K.0"	3315	2545	2453181	295.0	0.1124	0.1105	0.00026	225.0
"C2H6_PURE_270K.0"	3315	2545	2453181	270.0	0.1002	0.0996	0.00026	225.0
"C2H6_PURE_250K.0"	3315	2545	2453181	250.0	0.0901	0.0896	0.00026	225.0
"C2H6_PURE_215K.0"	3315	2545	2453181	215.0	0.0765	0.0763	0.00026	225.0
"C2H6_PURE_197K.0"	3315	2545	2453181	197.0	0.0689	0.0682	0.00026	225.0
"Ethane_300K.0000"	3310	2950	605332	293.0	0.5000	0.4058	0.00026	225.0
"Ethane_270K.0000"	3310	2950	605332	270.0	0.5000	0.4672	0.00026	225.0
"Ethane_250K.0000"	3310	2950	605332	252.0	0.5000	0.4367	0.00026	225.0
"Ethane_215K.0000"	3310	2950	605332	217.0	0.3824	0.3326	0.00026	225.0
"Ethane_195K.0000"	3310	2950	605332	195.0	0.2534	0.1954	0.00026	225.0
"C2H6_297K_763.48Torr.0"	3315	2545	613296	297.0	763.4800	0.3058	0.00026	60.0
"C2H6_296K_371.71Torr.0"	3315	2545	613296	296.0	371.7100	0.3066	0.00026	60.0
"C2H6_270K_601.36Torr.0"	3315	2545	613296	270.0	601.3600	0.3024	0.00026	60.0
"C2H6_270K_376.54Torr.0"	3315	2545	613296	270.0	376.5400	0.3029	0.00026	60.0
"C2H6_250K_626.45Torr.0"	3315	2545	613296	250.0	626.4500	0.2974	0.00026	60.0
"C2H6_250K_400.68Torr.0"	3315	2545	613296	250.0	400.6800	0.2896	0.00026	60.0
"C2H6_250K_200.10Torr.0"	3315	2545	613296	250.0	200.1000	0.3066	0.00026	60.0
"C2H6_215K_281.11Torr.0"	3315	2545	613296	215.0	281.1100	0.2375	0.00026	60.0
"C2H6_215K_206.91Torr.0"	3315	2545	613296	215.0	206.9100	0.4030	0.00026	60.0
"C2H6_215K_119.15Torr.0"	3315	2545	613296	215.0	119.1500	0.2389	0.00026	60.0
"C2H6_215K_049.44Torr.0"	3315	2545	613296	215.0	49.4400	0.2372	0.00026	60.0
"C2H6_194K_103.86Torr.0"	3315	2545	613296	194.0	103.8600	0.2208	0.00026	60.0
"C2H6_195K_076.35Torr.0"	3315	2545	613296	195.0	76.3500	0.2220	0.00026	60.0
"C2H6_195K_052.13Torr.0"	3315	2545	613296	195.0	52.1300	0.2208	0.00026	60.0

Empirical Pseudo-Linelist

Contains no spectroscopic insights

Basically a way of interpolating/extrapolating in P/T/ν between the various laboratory data.

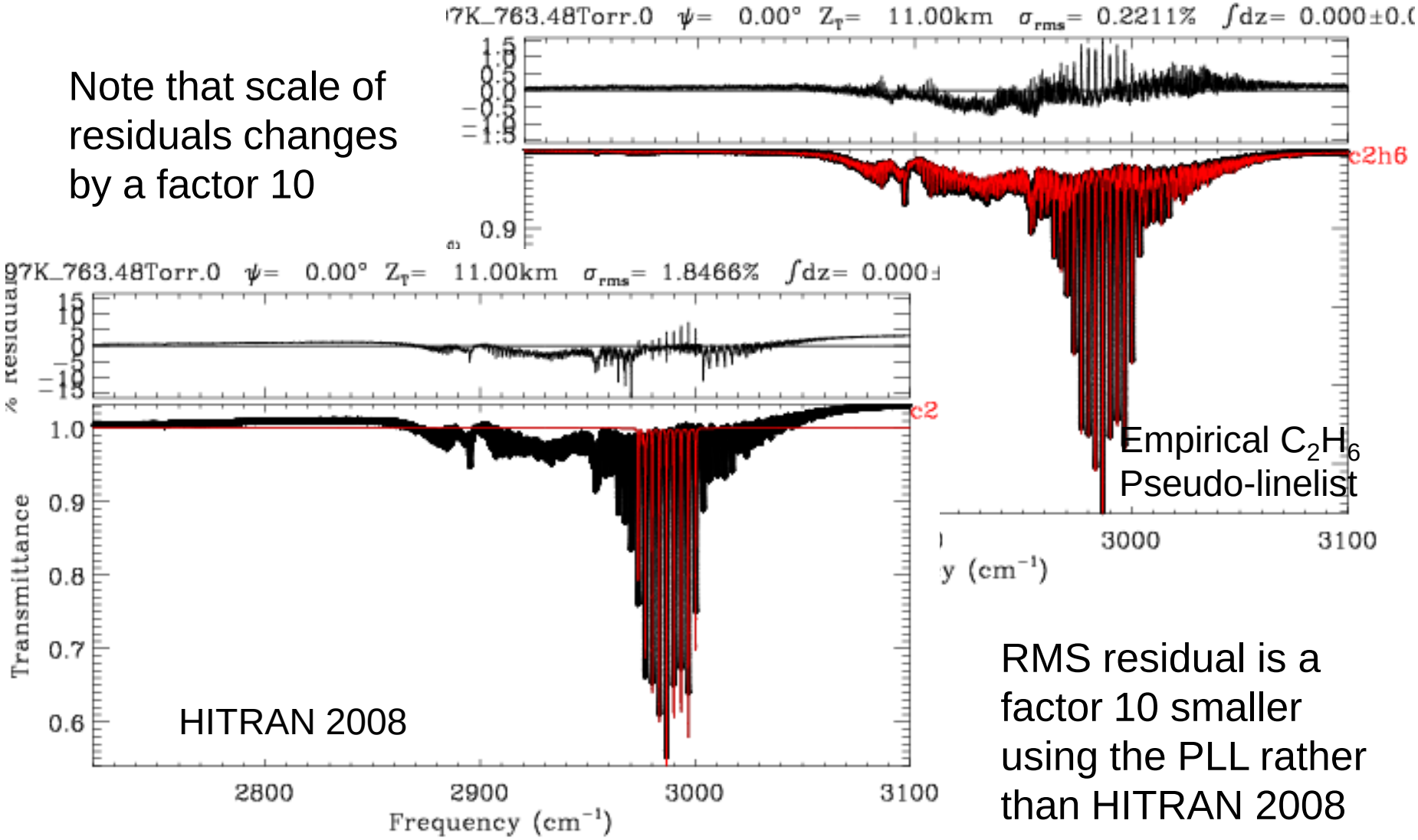
Uses a Voigt lineshape as a basis function

Extrapolates more accurately in P/T than polynomial

Fitting the lab spectra during the derivation of the PLL provides opportunity to account for ILS, contamination, zero-level offsets, etc and to identify/correct any outliers.

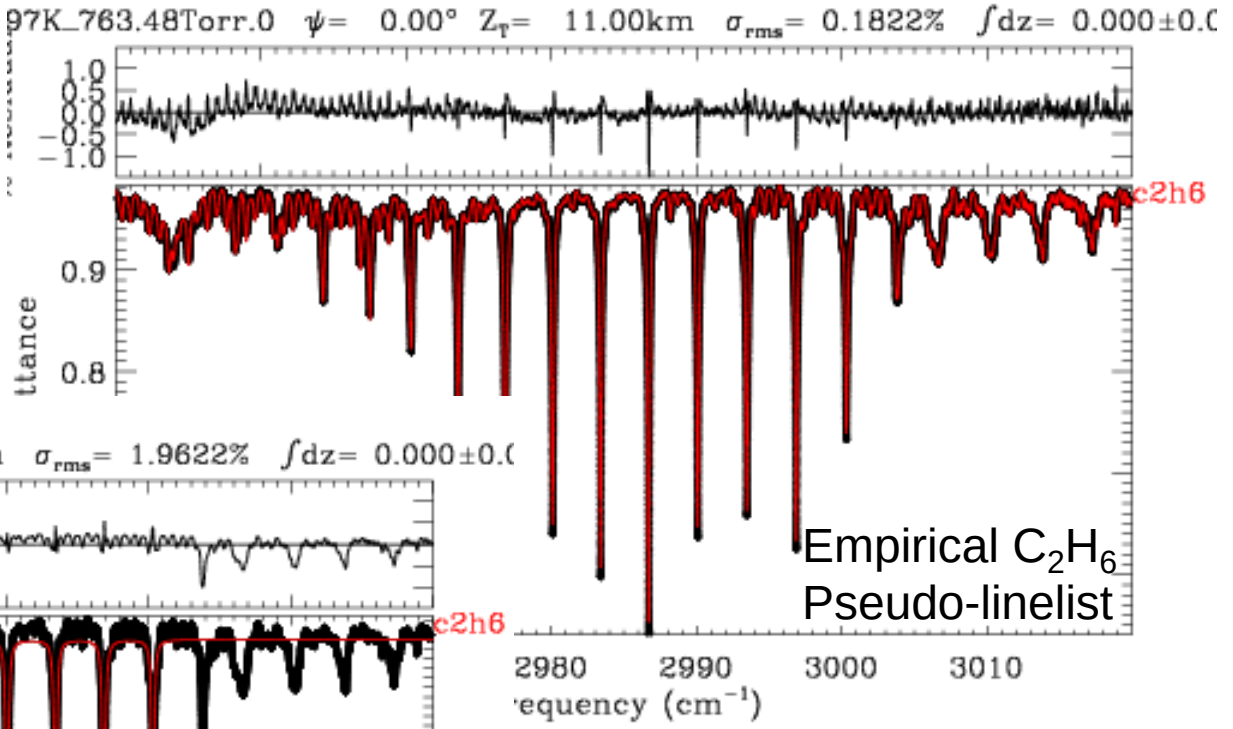
C_2H_6 lab spectrum: 1 atm, 297K

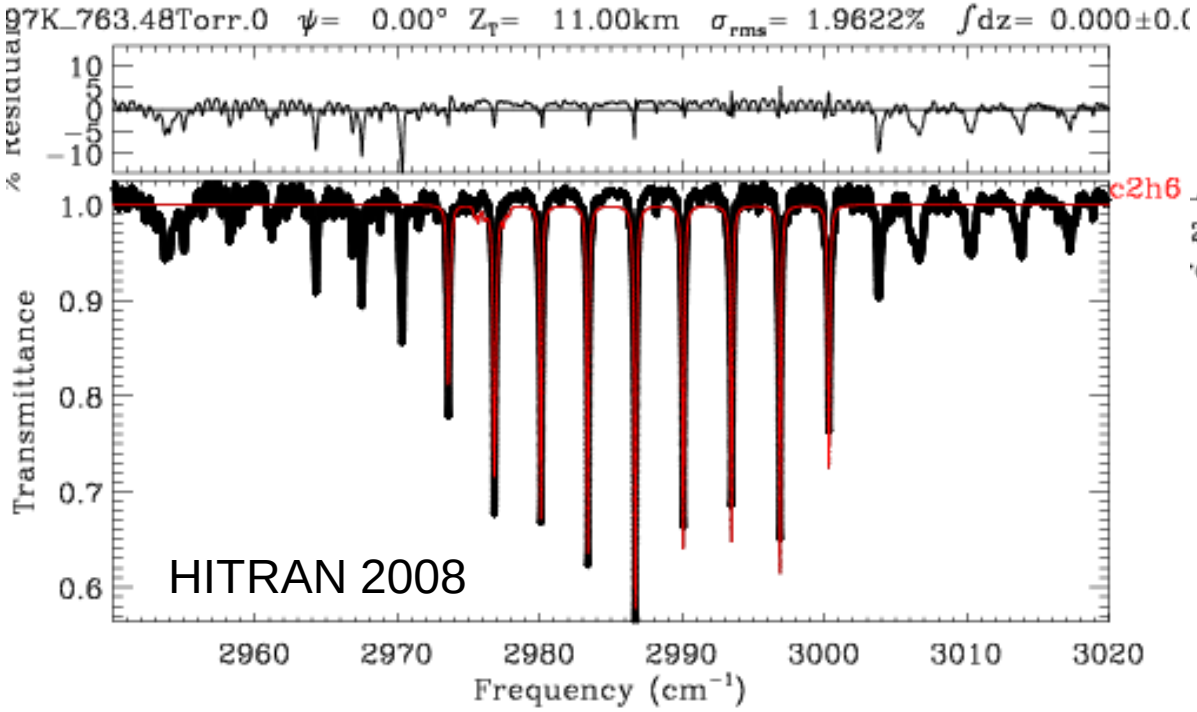
Note that scale of residuals changes by a factor 10



RMS residual is a factor 10 smaller using the PLL rather than HITRAN 2008

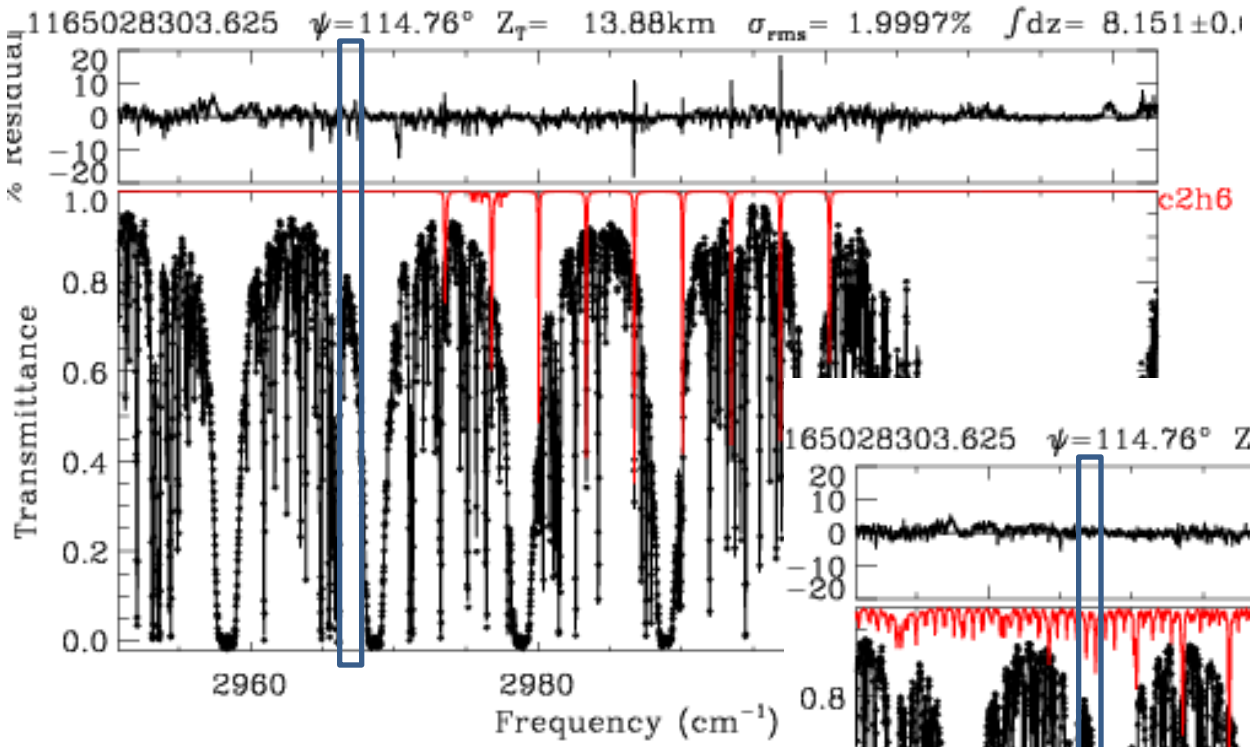
Zoom into region of PQ branches





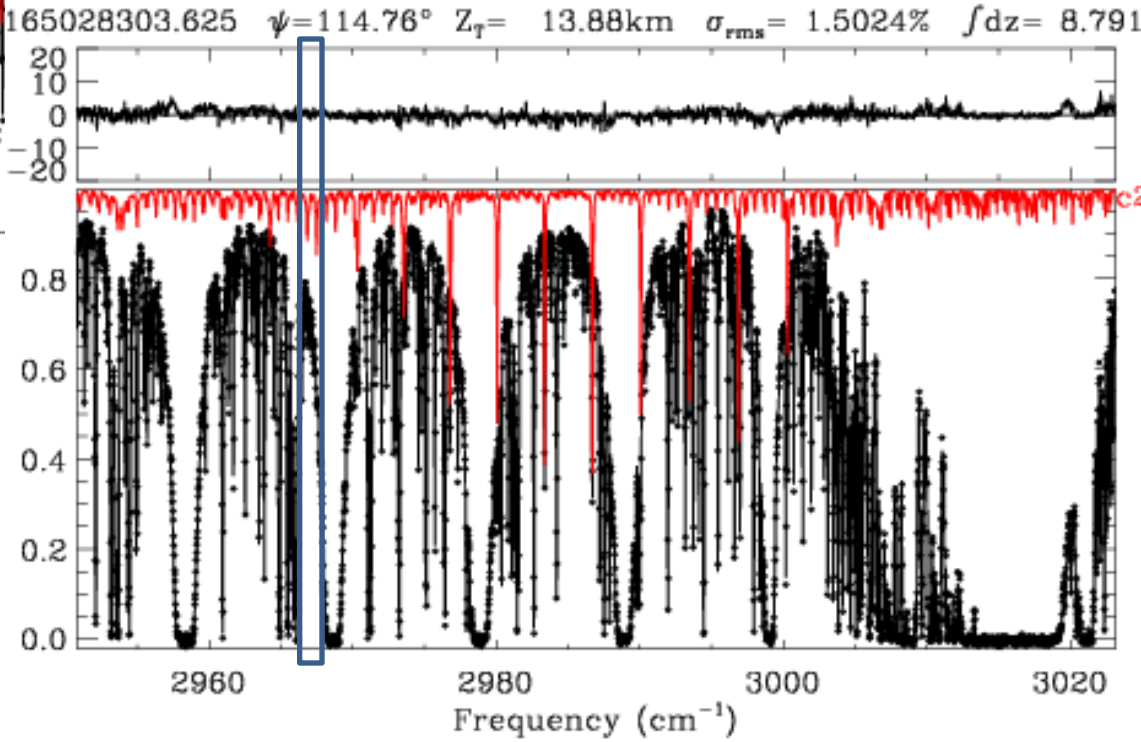
Comparison is unfair: it includes features not covered by HITRAN 2008 C_2H_6 linelist

Fits to an ACE spectrum at 14 km

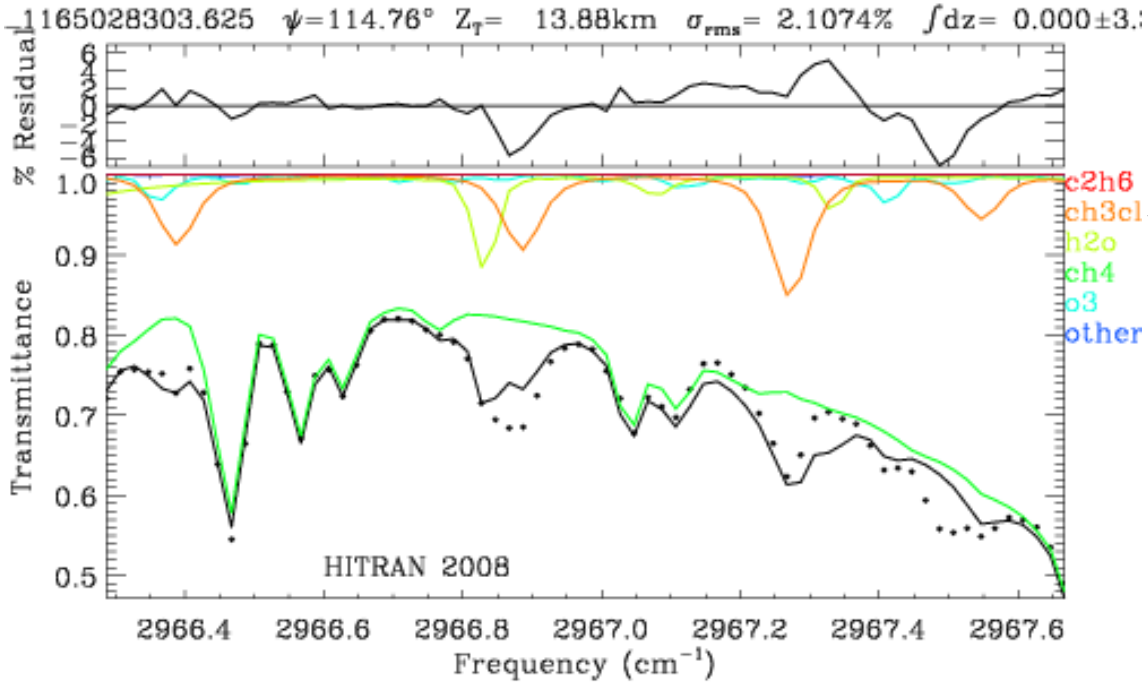


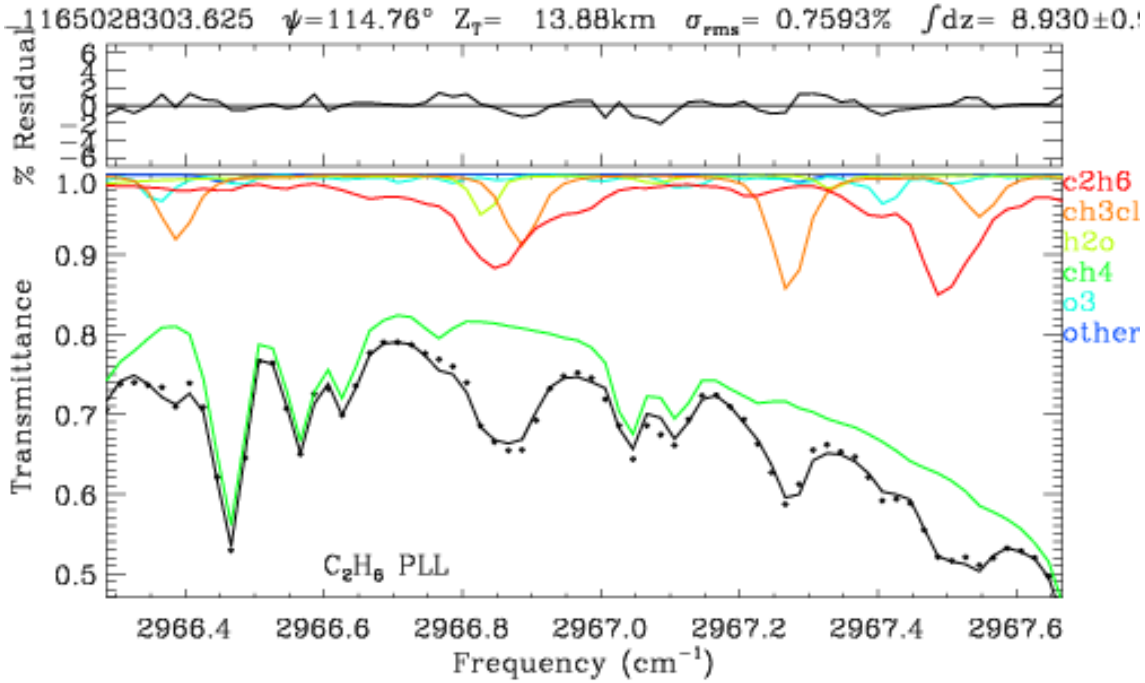
Left: HITRAN 2008

Below: Empirical C_2H_6 pseudo-linelist



Blue rectangle denotes window used for CH_3Cl retrievals





Impact of empirical C_2H_6 pseudo-lines on ACE spectral fits of CH_3Cl

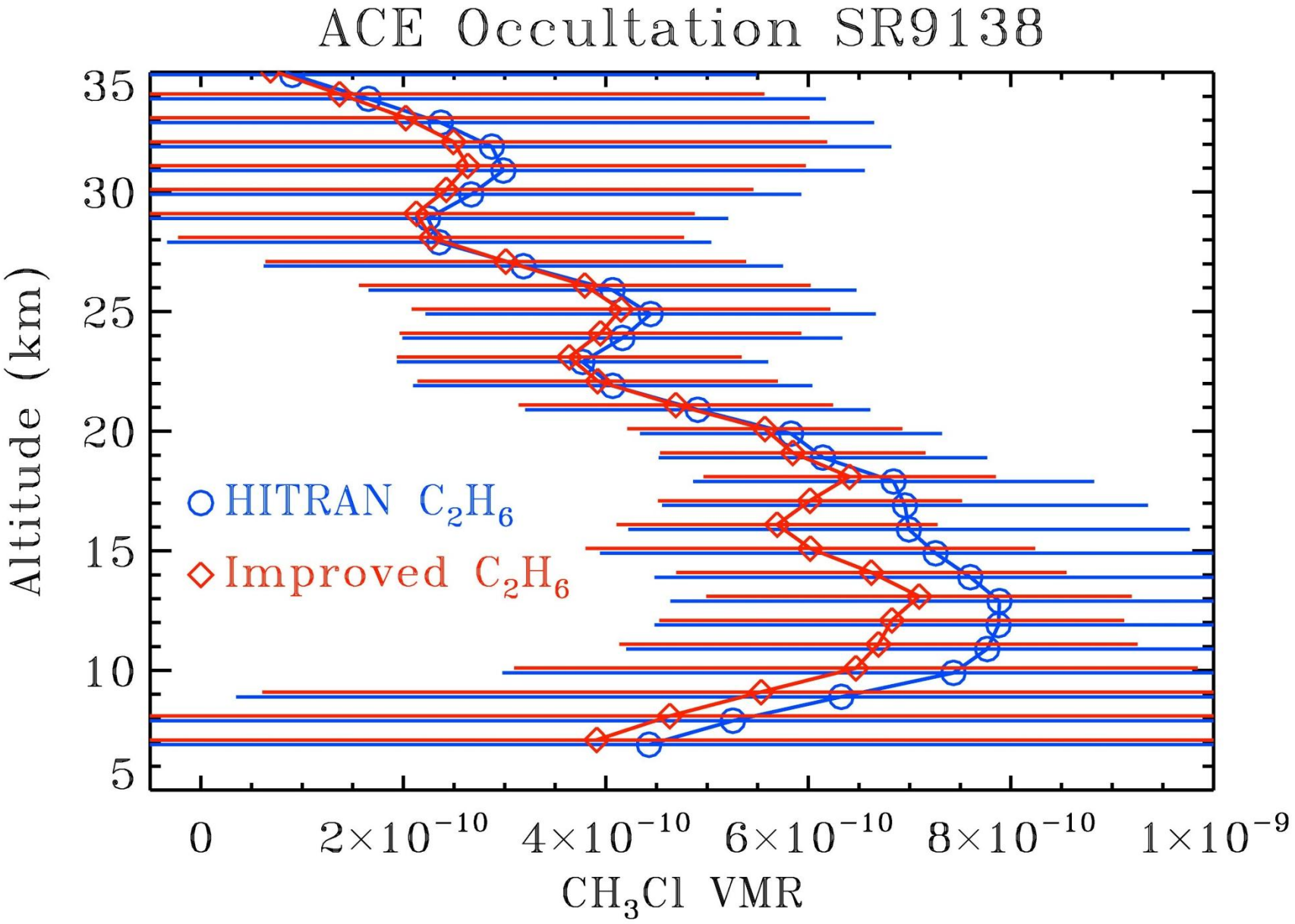
No C_2H_6 absorption lines in this interval.

Large systematic residuals due to missing C_2H_6 lines

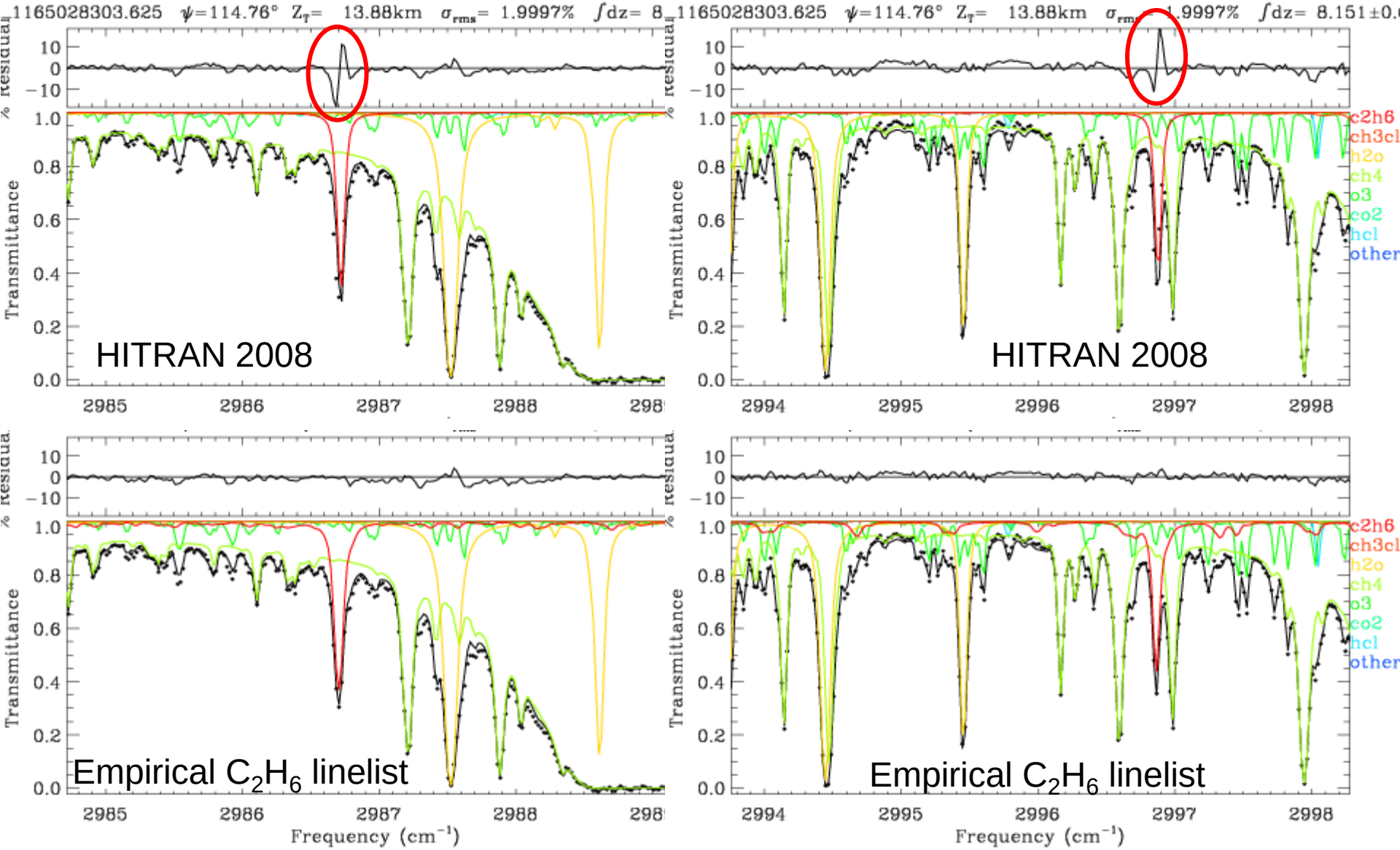
Using empirical C_2H_6 pseudo-lines instead of HITRAN 2008 lines.

RMS residual is reduced by nearly a factor 3

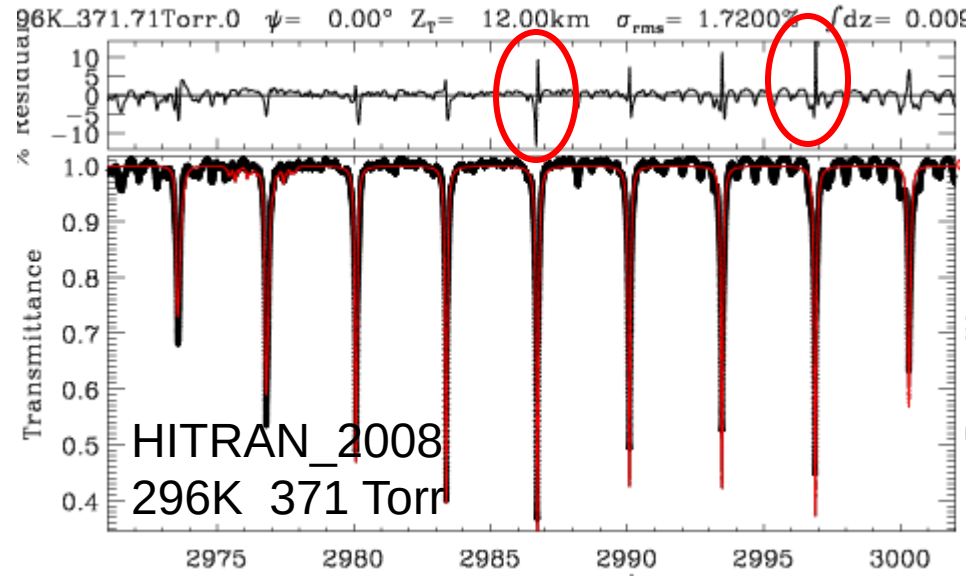
Impact on Retrieved CH_3Cl profiles

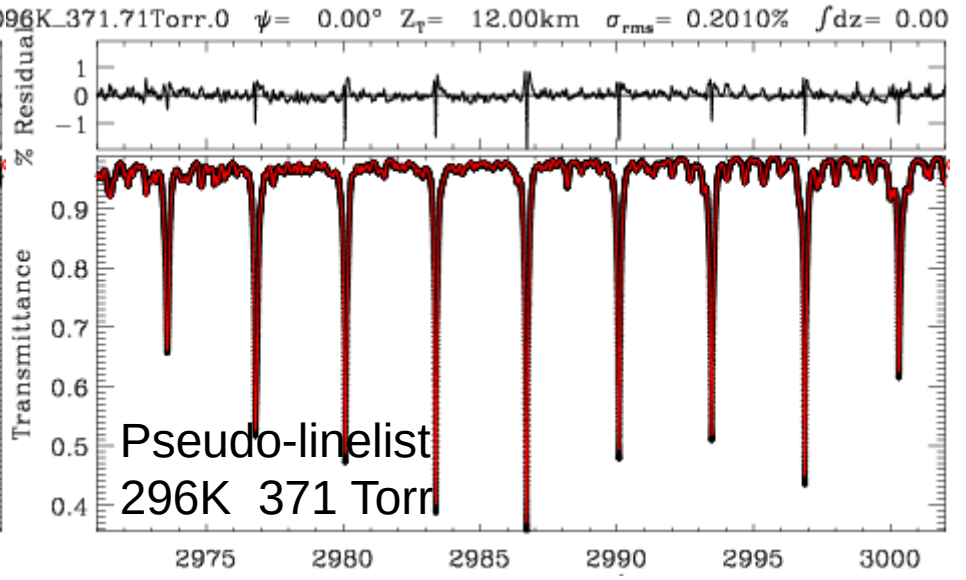


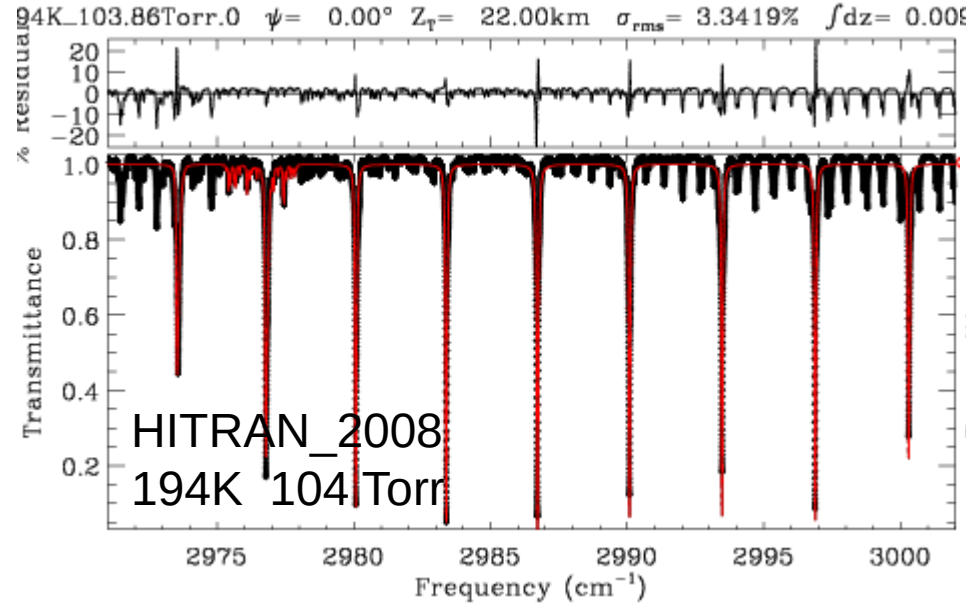
Fits to the worst PQ-branches

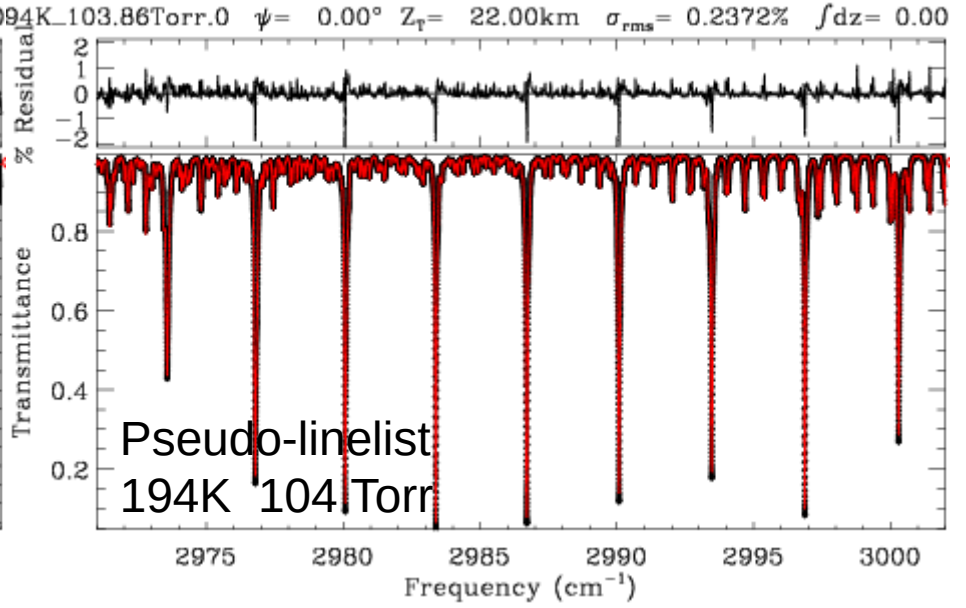


Fits to RAL spectra over HITRAN region









Fits to the PQ_3 C_2H_6 Q-branch at 2976.8 cm^{-1}

This Q-branch has a proper quantum-mechanically-derived linelist in HITRAN 2008 (Pine & Rinsland, 1999)

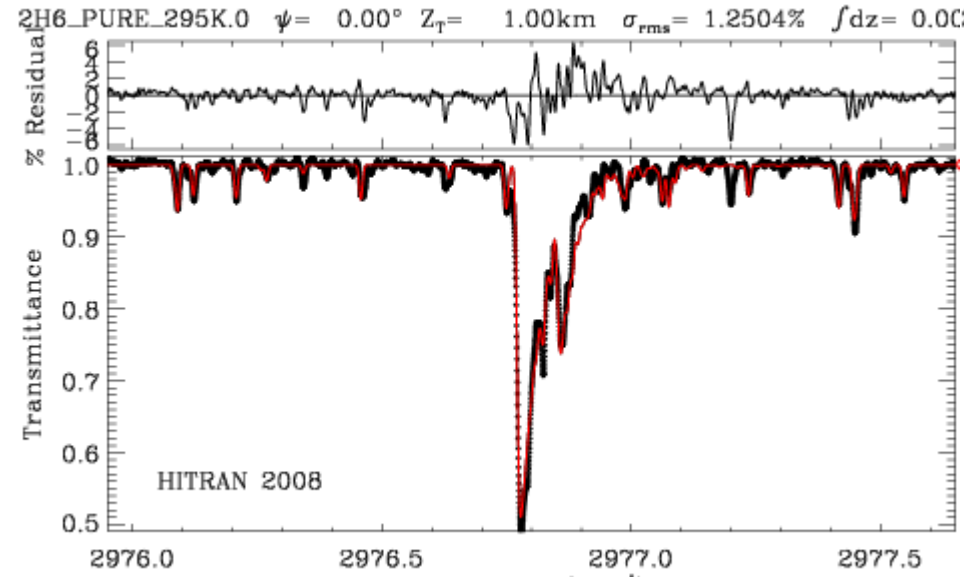
Let's see how fits to the narrow 2976.8 cm-1 region compare.

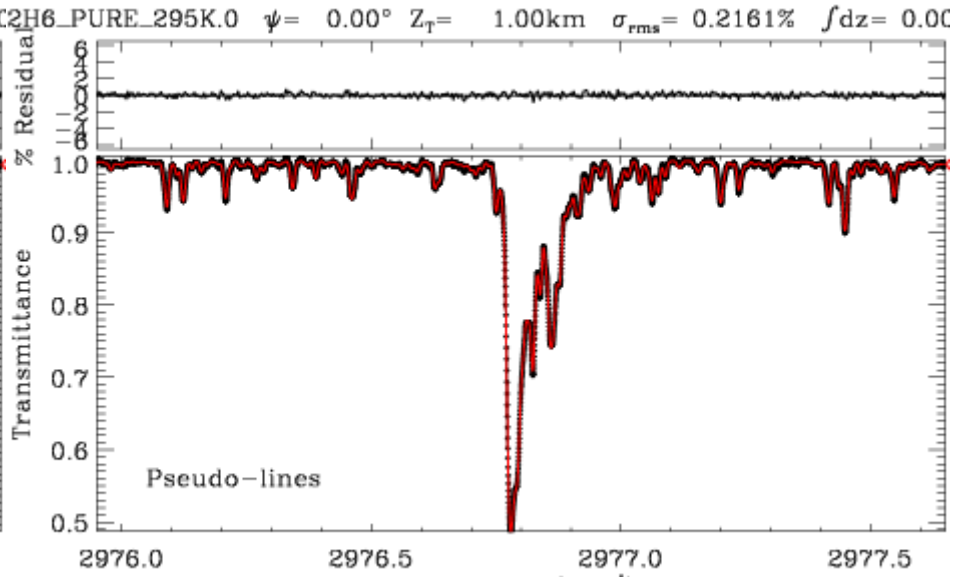
On following plots,
Left-hand panels show fits using HITRAN 2008 linelist
Right-hand panels show fit to same spectra but using pseudo-lines.

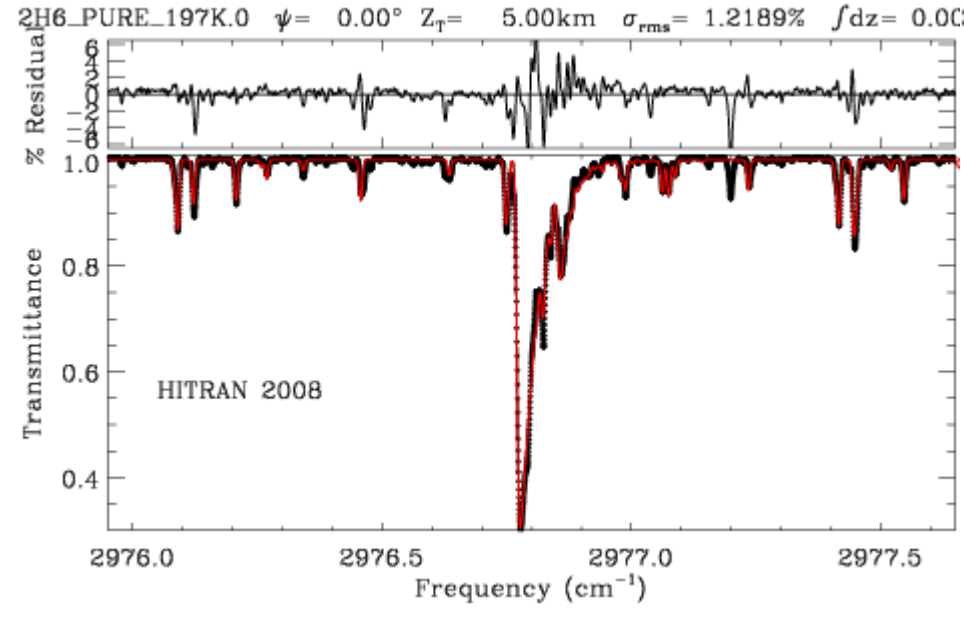
Top panels show room temperature spectra
Bottom panels show low temperature (197K) spectra

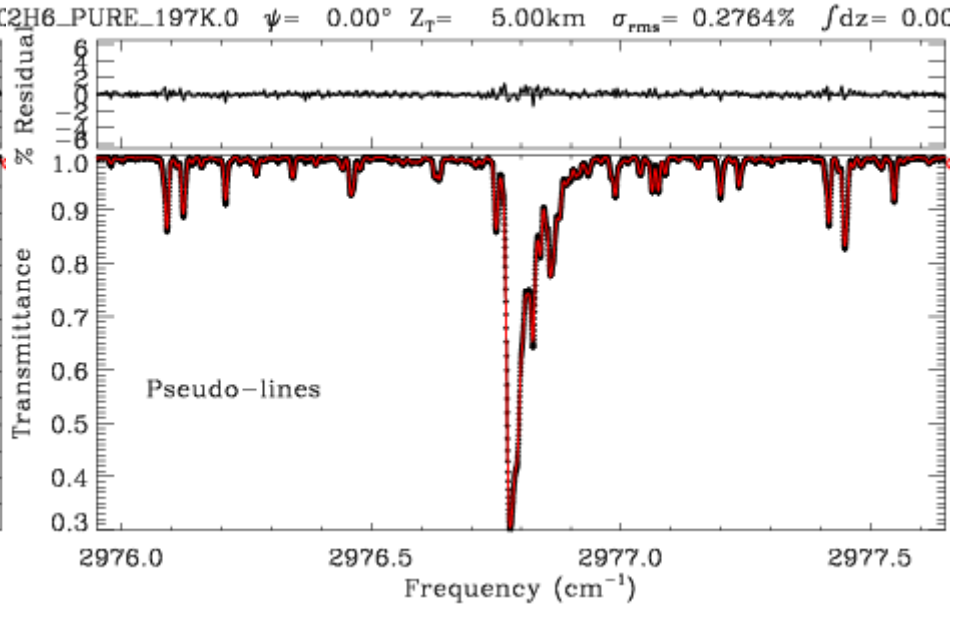
First page shows pure gas spectra
Second page shows air-broadened spectra

Pure C_2H_6

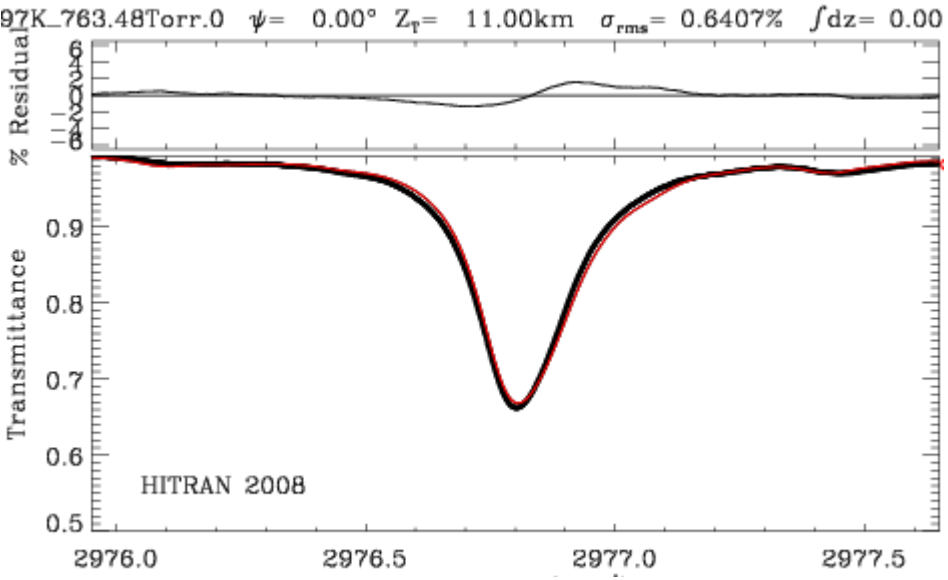

2H6_PURE_295K.0 ψ= 0.00° Z_T= 1.00km σ_rms= 1.2504% ∫dz= 0.00
% Residual
Transmittance
HITRAN 2008
2976.0
2976.5
2977.0
2977.5

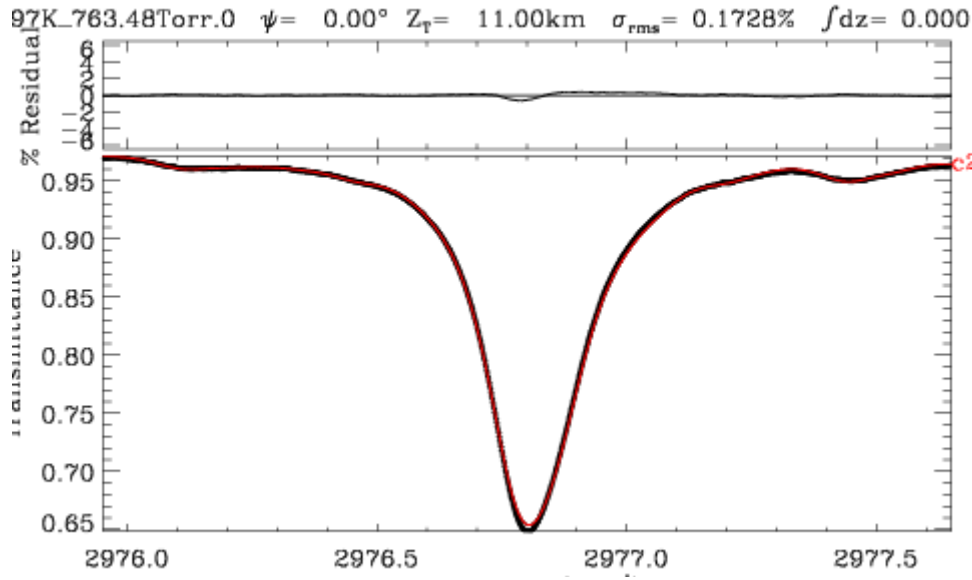

2H6_PURE_295K.0 ψ= 0.00° Z_T= 1.00km σ_rms= 0.2161% ∫dz= 0.00
% Residual
Transmittance
Pseudo-lines
2976.0
2976.5
2977.0
2977.5

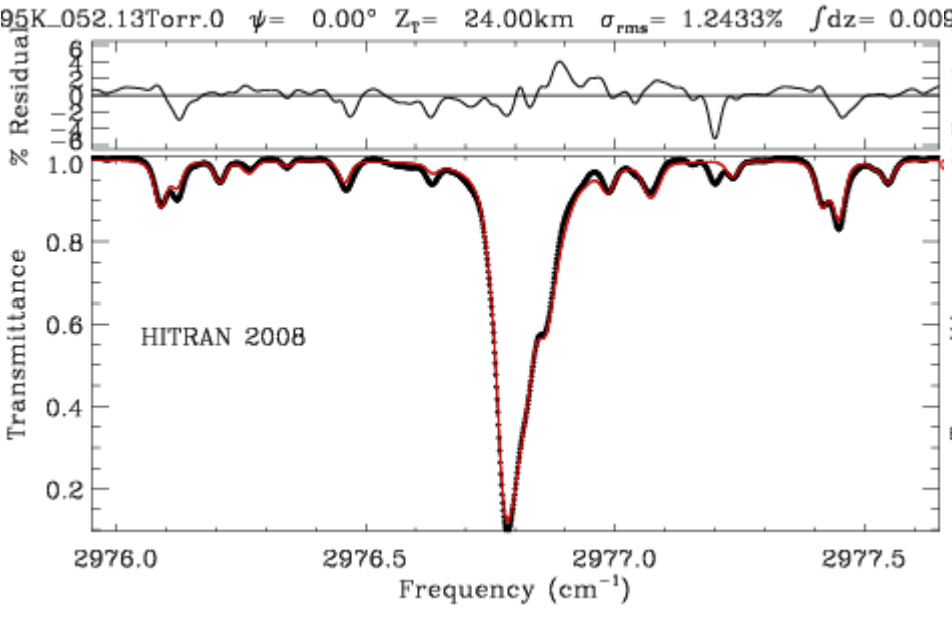

2H6_PURE_197K.0 ψ= 0.00° Z_T= 5.00km σ_rms= 1.2189% ∫dz= 0.00
% Residual
Transmittance
HITRAN 2008
2976.0
2976.5
2977.0
2977.5
Frequency (cm⁻¹)

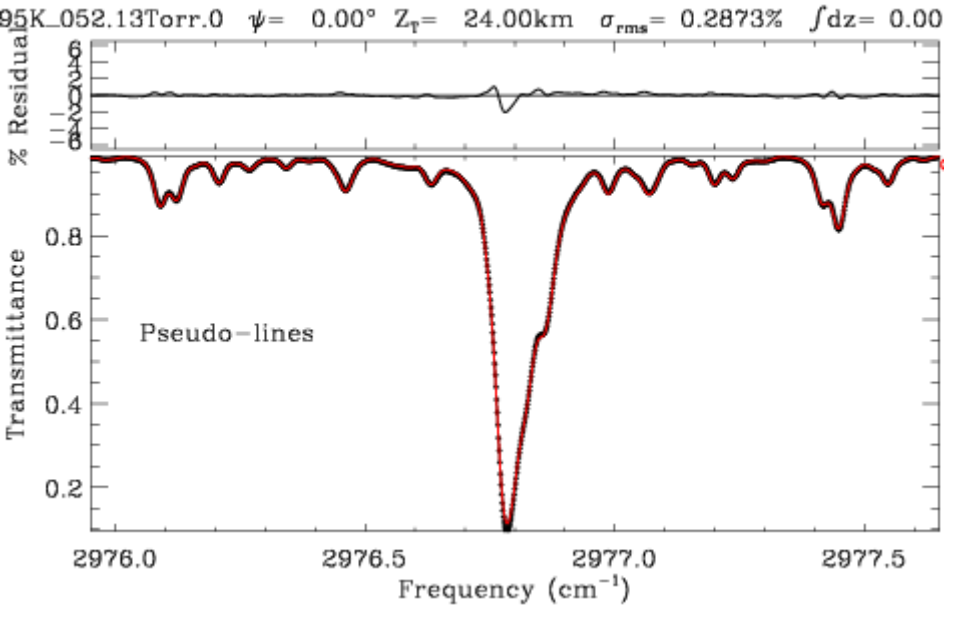

2H6_PURE_197K.0 ψ= 0.00° Z_T= 5.00km σ_rms= 0.2764% ∫dz= 0.00
% Residual
Transmittance
Pseudo-lines
2976.0
2976.5
2977.0
2977.5
Frequency (cm⁻¹)

Air-broadened C_2H_6





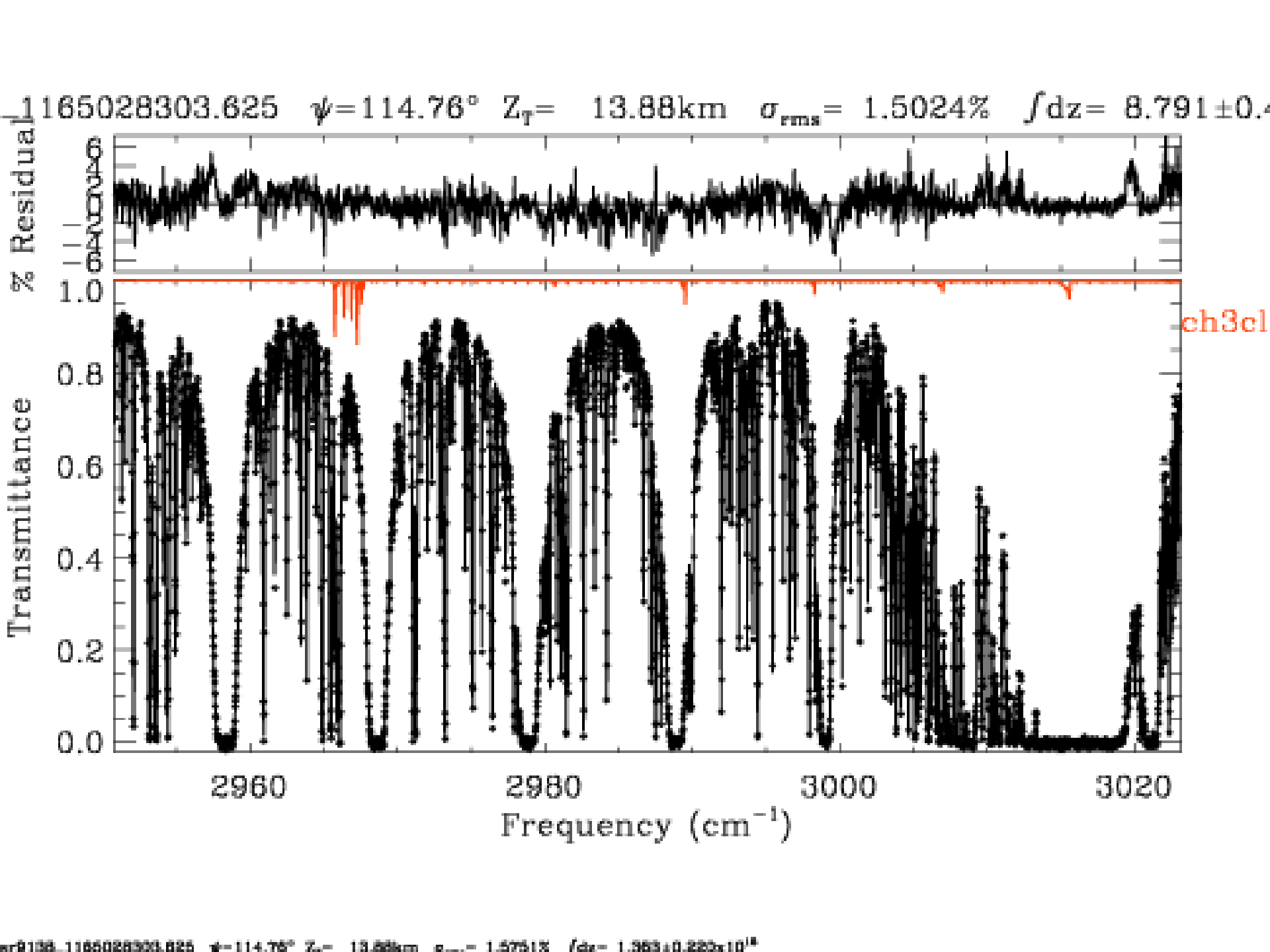




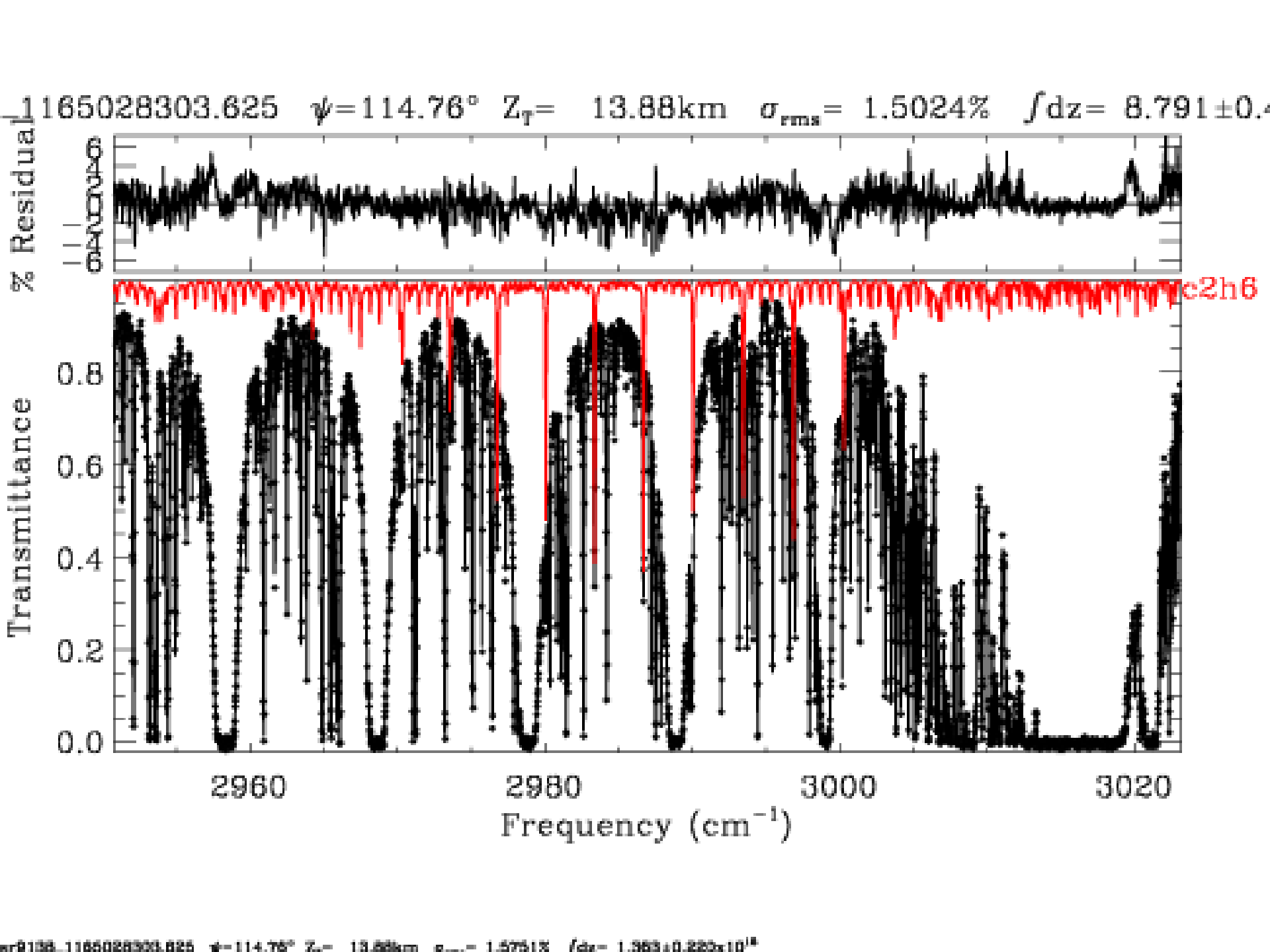
Summary

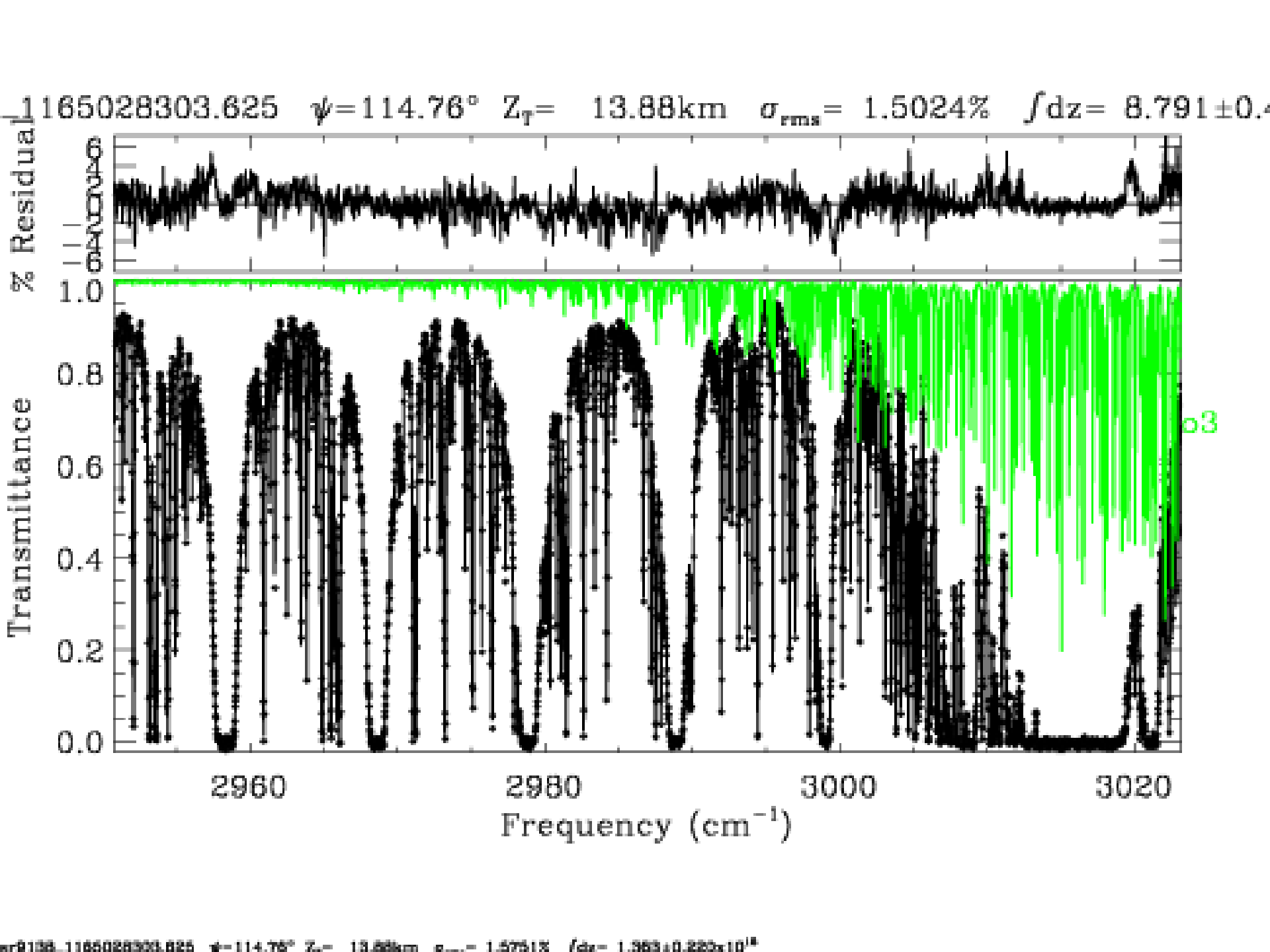
- In atmospheric spectra, the 2850-3050 cm^{-1} region contains absorptions from many gases of interest (e.g. everything having a C-H stretch).
- This interval also contains the strongest infrared absorptions of C_2H_6, which can exceed 50% in depth in limb spectra of the tropical troposphere.
- Although the July 2007 HITRAN C_2H_6 update captures the 9 strongest C_2H_6 PQ-branches, it omits all of the weaker absorptions features.
- Quantum-mechanical analysis of the C_2H_6 spectrum is very difficult and therefore lacking, with the exception of the PQ_3 branch.
- As a temporary fix, an empirical C_2H_6 pseudo-linelist (PLL) has been developed based on laboratory measurements by Harrison et al. [2010].
- Use of this PLL results in much smaller residuals to fits to lab spectra and to atmospheric spectra (e.g. ACE) and can significantly improve retrievals of other minor gases (e.g. CH_3Cl).

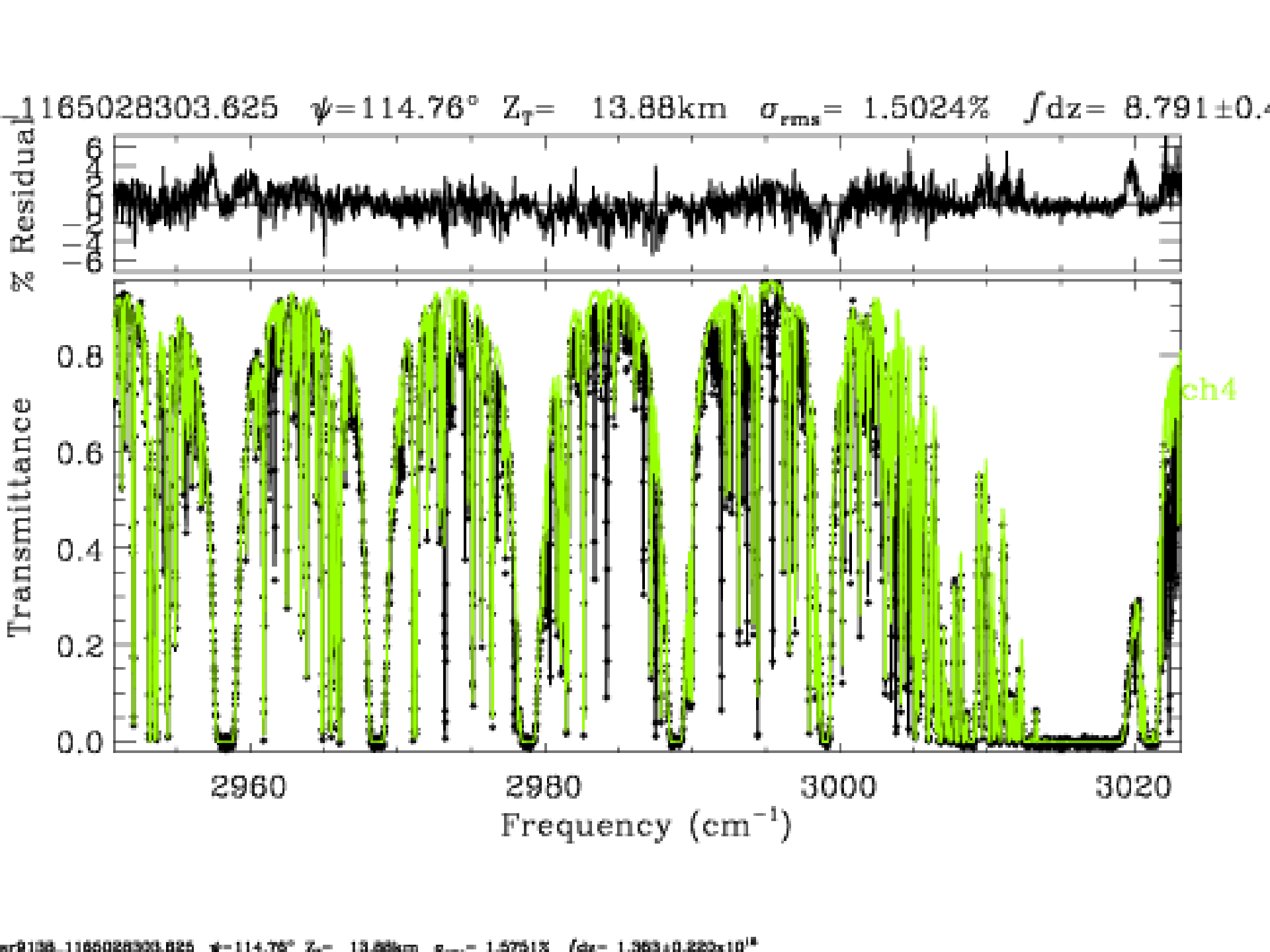
Supplemental Material



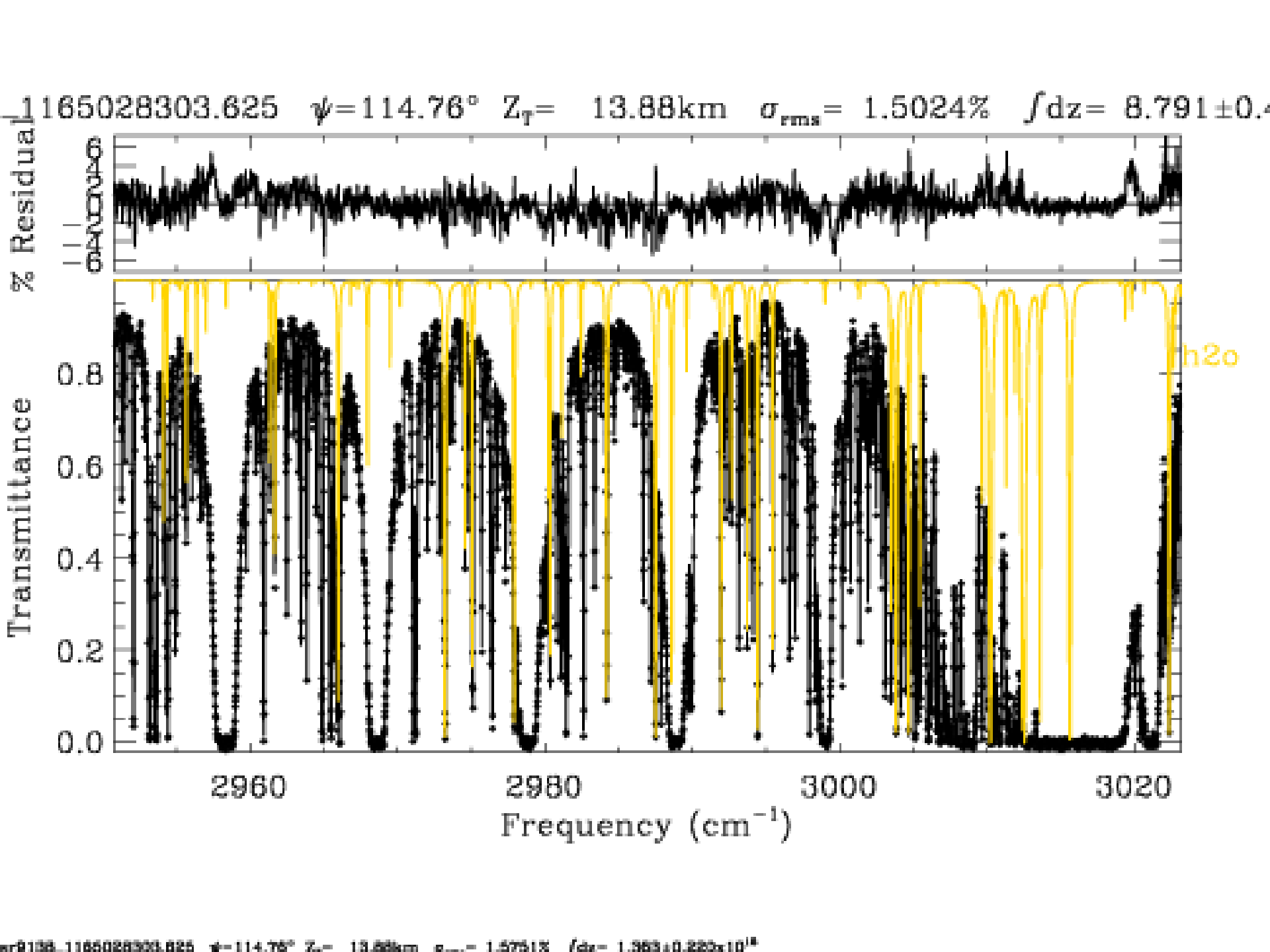
er9138_1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5751% ∫dz= 1.383±0.220x10^18


1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5024% ∫dz= 8.791±0.4
% Residual
6
4
2
0
-2
-4
-6
c2h6
Transmittance
0.0
0.2
0.4
0.6
0.8
2960
2980
3000
3020
Frequency (cm^-1)

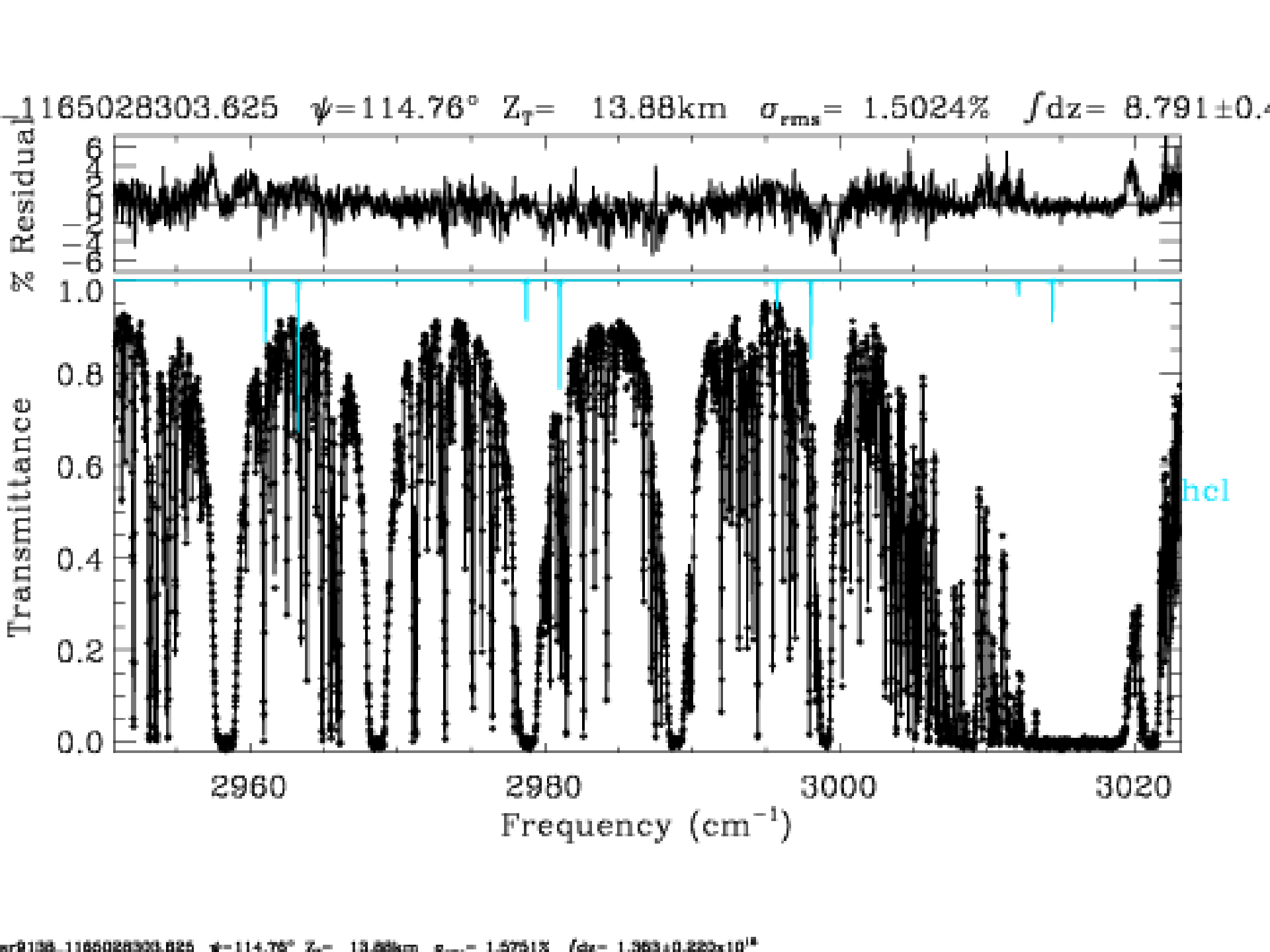

1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5024% ∫dz= 8.791±0.4
% Residual
6
4
2
0
-2
-4
-6
Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
o3
2960
2980
3000
3020
Frequency (cm^-1)

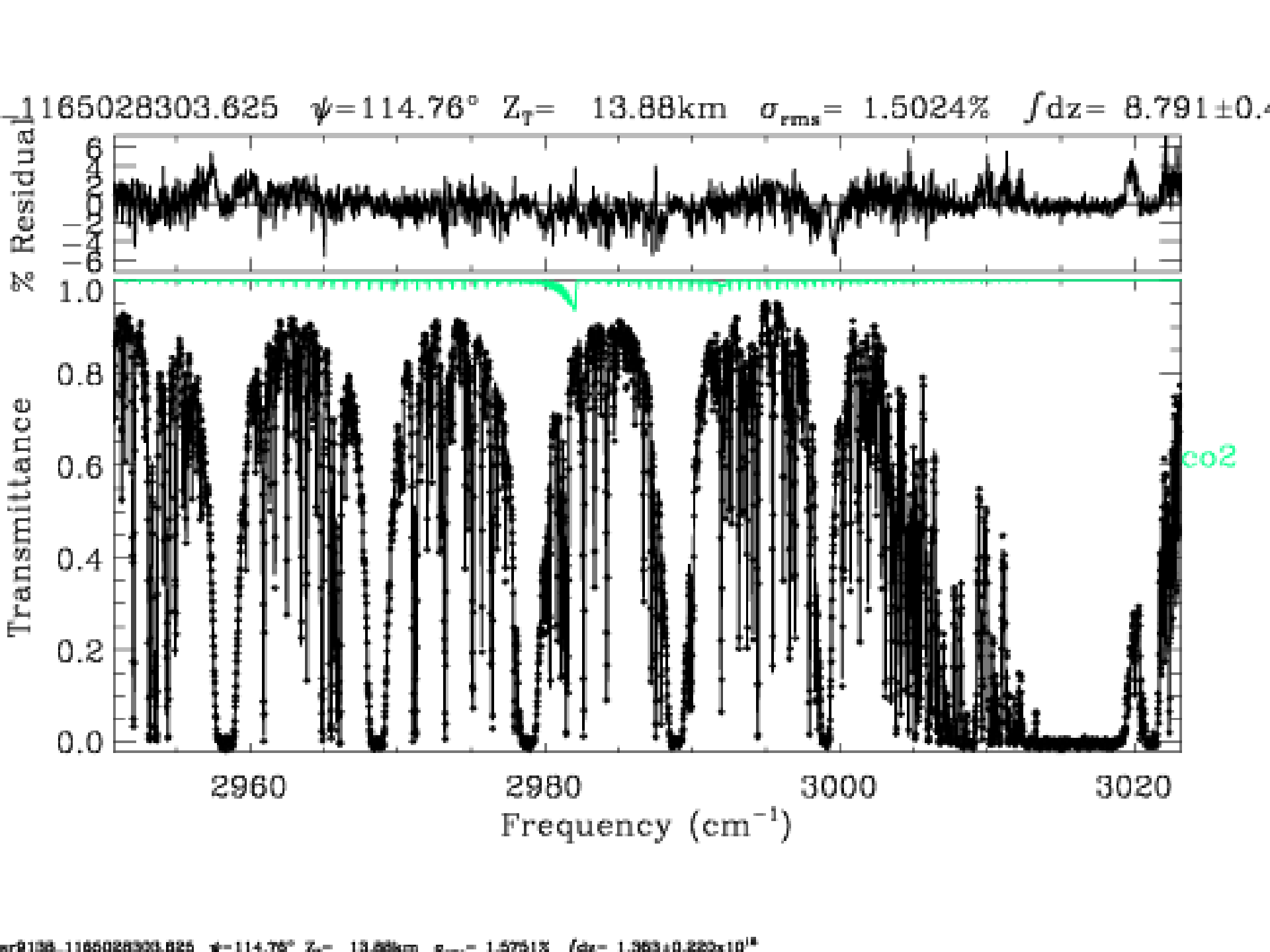


er9138_1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5751% ∫dz= 1.363±0.220x10^18



er9138_1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5751% ∫dz= 1.383±0.220x10^18


1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5024% ∫dz= 8.791±0.4
% Residual
6
4
2
0
-2
-4
-6
Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
hcl
2960
2980
3000
3020
Frequency (cm^-1)


1165028303.625 ψ=114.76° Z_T= 13.88km σ_rms= 1.5024% ∫dz= 8.791±0.4
% Residual
6
4
2
0
-2
-4
-6
Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
co2
2960
2980
3000
3020
Frequency (cm^-1)

Derivation of Empirical Linelist

1) Initialize pseudo-linelist using low-pressure, room-T spectra
- Find line positions based on third-derivative of measured spectrum
- Assign strengths based on absorption depth
- Assign E”=300 cm^{-1}
- Assign widths: ABHW=0.06 cm^{-1}/atm, SBHW=0.12 cm^{-1}/atm

2) Fit the laboratory spectra using a full-physics spectral fitting algorithm.

3) Calculate improved intensities (S) and ground-state energies (E”) for each line based on spectral fits to the lab spectra. Go to (2)

4) Use air-broadened spectra to develop an improved ABHW, perhaps assuming an empirical relationship between ABHW and E”. Go to (2)

Automated adjustment of S and E”

Tc is calculated transmittance spectrum using current value of S(296) and E”
Tm is the measured transmittance spectrum

$T_{i,j}c = \exp[-X_j \cdot S_i^c(296) \cdot (296/T_j)^{\beta} \cdot \exp (hcE''^c_i(1/296 - 1/T_j)]$

$T_{i,j}m = \exp[-X_j \cdot S_i^m(296) \cdot (296/T_j)^{\beta} \cdot \exp (hcE''^m_i(1/296 - 1/T_j)]$

i= index over spectral lines, j= index over measured spectra

$\text{Log}_e[T_c] = -X_j \cdot S_i^c(296) \cdot (296/T_j)^{\beta} \cdot \exp (hcE''^c_i(1/296 - 1/T_j)$

$\text{Log}_e[T_m] = -X_j \cdot S_i^m(296) \cdot (296/T_j)^{\beta} \cdot \exp (hcE''^m_i(1/296 - 1/T_j)$

$\text{Log}_e[T_c] / \text{Log}_e[T_m] = S_i^c(296)/ S_i^M(296) \cdot \exp (hc.(E''^c_i - E''^m)(1/296 - 1/T_j)$

$\log_e(\log_e[T_c]/\log_e[T_m]) = \log_e(S_i^c(296)/ S_i^M(296)) + (hc(E''^c_i - E''^m_i).(1/296 - 1/T_j)$

Plot $hc(1/296 - 1/T_j)$ versus $\log_e(\log_e[T_c]/\log_e[T_m])$ for the different measurement conditions and fit a straight line to the points:

- The intercept = $\log_e(S_i^c(296)/ S_i^M(296))$ is the error in the intensity
- The slope is the error in the assumed ground-state energy (E''^c)

If points do not fall on a straight line, this indicates a problem.
This line fitting is done for every frequency point or spectral line.

Conclusions

Over the 2971 – 3002 cm-1 region covered by HITRAN, the PLL produces spectral fits to lab spectra that are typically a factor 5-10 times better than HITRAN.

Even in the PQ_3 branch, for which HITRAN has a “proper” linelist, the PLL produces fits which are 5x better than HITRAN.

This should be no surprise. The pseudo-lines were derived from the lab spectra being fitted

Why doesn’t the PLL fit the lab spectra perfectly?
The fit is over-determined: 27 spectra; only 2 parameters fitted(S, E”)

Why not also fit the widths of each line individually?

- Many of the lines are overlapping - need a priori constraints
- The low-T measurements are all at low pressure – little info on T-dependence